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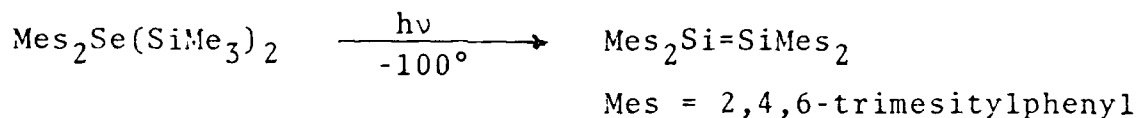
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In this report, research on four major aspects of our general program will be summarized:

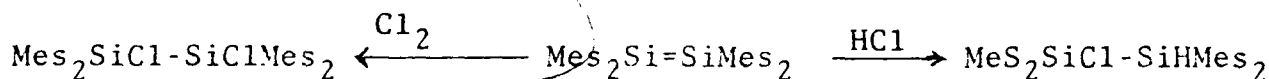
1) Disilene Chemistry; 2) Disilabenzene; 3) polysilastyrene and other Silane-High Polymers; 4) Cyclic Polysilanes.

1) Disilene Chemistry (In collaboration with Prof. J. Michl, Univ. of Utah).

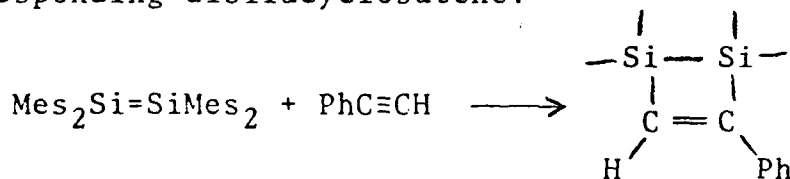
In December of 1982 our initial report was published on tetramesityldisilene. The first compound containing a silicon-silicon double bond. Considerable national and international publicity arose from this breakthrough, which seemed likely to open a large new area of silicon chemistry. The key compound is made by photolysis of a trisilane precursor at -80°C :



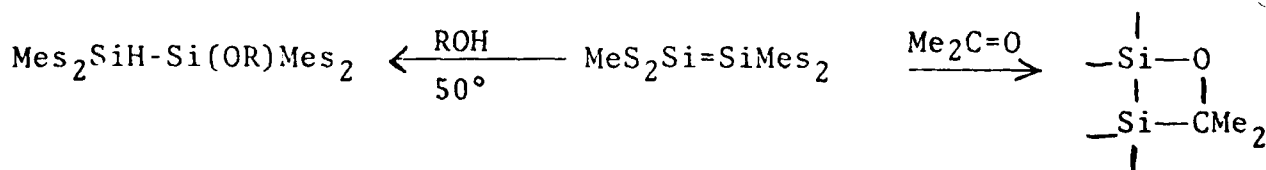
During the period covered by this report, a number of chemical reactions of tetramesityldisilene have been carried out. The compound behaves like an olefin in some reactions, for instance addition of hydrogen halides or chlorine.



It will also undergo cycloaddition with phenylacetylene to the corresponding disilacyclobutene.



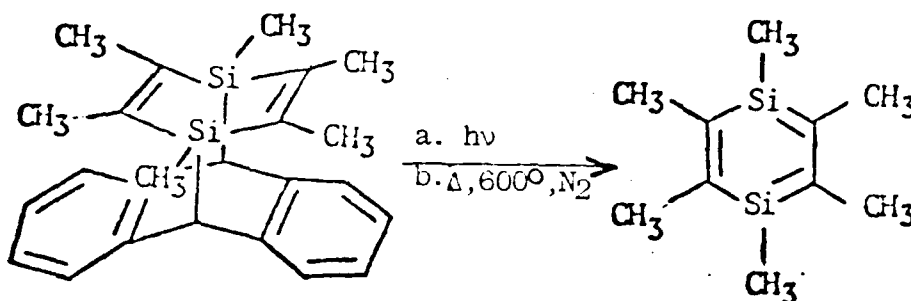
However other reactions are unprecedented for olefins, for instance the addition of alcohols and ketones to the Si=Si double bond.



Tetramesityldisilene also undergoes reduction easily to form a rather stable anion-radical. The structure of the parent compound has been determined by x-ray crystallography, which shows that the Si-Si bond is quite short (2.16 Å) consistent with considerable pi-bonding between the silicon atoms.

2) Disilabenzene.

During the past year we have obtained the first evidence for a benzene molecule containing two silicon atoms. Hexamethyl-1,4-disilabenzene. This compound was obtained by thermolysis or photolysis, of the precursor shown below:



3. Polysilastyrene and other Polysilane High Polymers

The synthesis of polysilastyrene has been systematically studied, and some of the variables in the process are now understood. Samples of various molecular weight can be produced, from quite low (~6000) to very high (400,000). The photolysis of polysilastyrene leads, depending on conditions, either to degradation or crosslinking. Photolysis can therefore be used to generate either positive or negative photoresists. Advantage is being taken of this process in the IBM laboratories in fabrication of silicon computer chips. Because polysilastyrene can be transformed into silicon carbide thermally, the photolytic activity makes it possible to "print" silicon carbide and a substrate. A film of polysilane is deposited on a ceramic or metal and exposed to ultraviolet light through a mask. Solvent removes the polymer from unexposed areas, the exposed, crosslinked polymer remains on the substrate. Heating then transforms the polymer to silicon carbide.

4. Cyclic Polysilanes.

A number of advances have been made in this continuing area of our research:

a) The cyclic phenylmethylsilane isomers $(\text{PhMeSi})_6$, have been separated and identified.

b) The ethylmethylcyclosilanes, $(\text{EtMeSi})_n$, have been synthesized and studied. Chromatography of this mixture provides evidence for the largest cyclosilane ring yet known, $(\text{EtMeSi})_{42}$.

c) Two series of silicon rotanes have been synthesized, $[(CH_2)_5Si]_n$ (n = 4-6) and $[(CH_2)_4Si]_n$ n = 5-20.

d) Detailed investigations of the electron spin resonance of anion-radicals of many new cyclosilanes have been carried out.

d) The four-membered ring compound $(Et_2Si)_4$ has been shown to have exceptional chemical reactivity, and to undergo numerous olefin-like reactions.

Most of these problems are still under continuing investigation.

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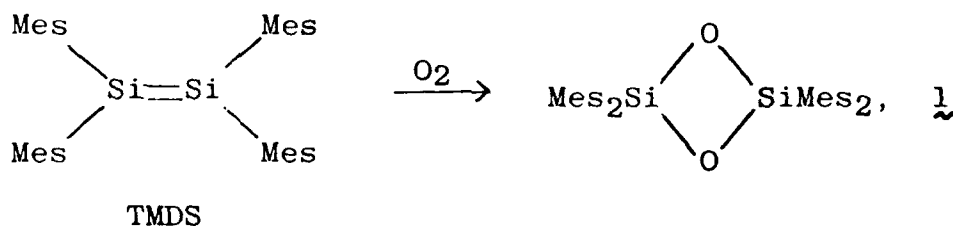
Period Covered: August 1, 1982 - December 31, 1982

During the five months covered by this report, progress has been made in the areas of both polymeric and monomeric silanes. Our research on small molecules will be covered first, followed by work on polymers.

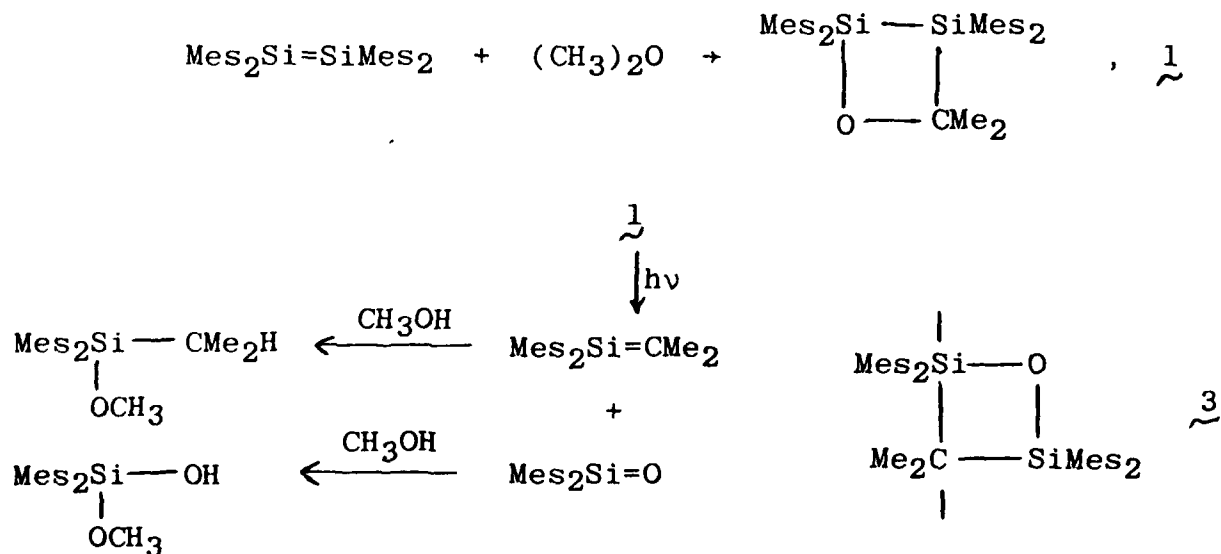
A) Silicon-Silicon Double Bonds

Tetramesityldisilene (TMDS), the first substance containing a silicon-silicon double bond, was reported from our laboratories in 1981. Additional chemical reactions of TMDS have been investigated, and a second example of a silicon-silicon double bond has been isolated.

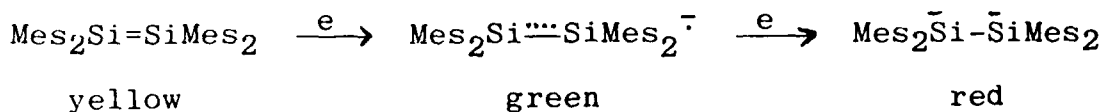
TMDS reacts spontaneously, although slowly, with oxygen. The product is the four-membered ring compound, 1. This compound is the first known example of a cyclic disiloxane.



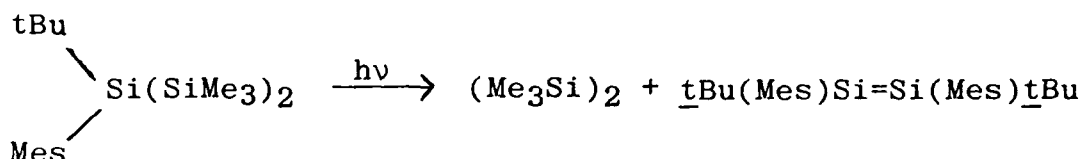
Photolysis of the acetone adduct of TMDS, 2, leads to a rearranged isomer, 3, with a structure similar to that of 1. This rearrangement was shown to proceed through formation of the multiply-bonded intermediates $\text{Mes}_2\text{Si}=\text{CMe}_2$ and $\text{Mes}_2\text{Si}=\text{O}$, which were trapped by reaction with methanol:



TMDS undergoes reduction electrolytically to a green anion-radical, and eventually to a red dianion. The nature of these species is under study.



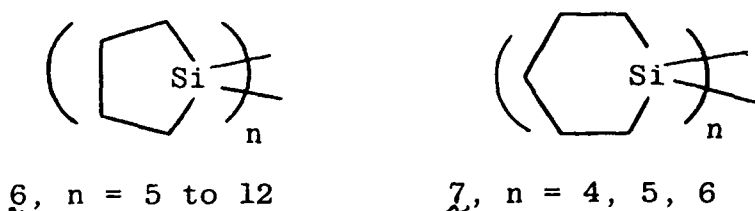
Photolysis of the trisilane precursor 4 leads to the second example of a disilene, 5. This pale yellow compound survives heating to >220°C, and therefore appears to be even more stable than TMDS. Only one isomer of 5 is formed, but



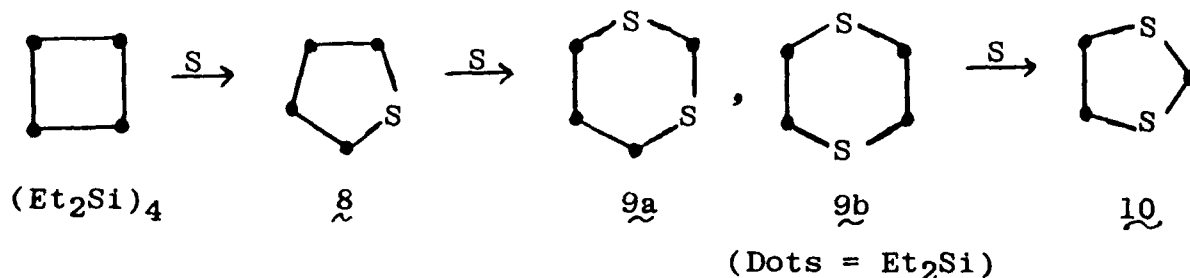
we are not yet certain whether this product is the cis or the trans isomer.

B) Cyclic Polysilanes

Characterization of two series of cyclic silanes, $(\text{Et}_2\text{Si})_n$ and $(\text{EtMeSi})_n$, has been completed and this work is being written up for publication. Research has similarly been completed on the two series of organosilicon rotanes, 6 and 7.



The labile compound $(\text{Et}_2\text{Si})_4$ reacts with sulfur at elevated temperatures forming first 8, then 9a and 9b, then 10:



Both Et_2Si and the interesting silane thione, $\text{Et}_2\text{Si}=\text{S}$, appear as intermediates in this sequence of reactions.

C) Polysilane Polymers

A large number of new homopolymers and copolymers in the polysilane family have been synthesized during the period of this report. These are summarized in Tables 1 and 2. All of these compounds are possible precursors for silicon carbide, and several of them are being studied industrially because of their photoactivity.

An important recent discovery is that polysilane polymers are excellent photocatalysts for the polymerization of vinyl monomers such as methyl acrylate and styrene.

Cumulative List of Publications

Publications from earlier AFOSR grant, AF-AFOSR-78-3570, not previously reported:

Synthesis and Properties of Substituted Methylcyclopoly-silanes, B. J. Helmer and R. West, J. Organometal. Chem., 236, 21-32 (1982).

Organopolysilanes, R. West in "Comprehensive Organometallic Chem." E. Abel (ed.), Pergamon Press Ltd., Oxford, England, 1982, Ch. 9.4, p. 365-397.

Organic Chemistry Based on Silicon: The Cyclic Permethyl-polysilanes, R. West, China-Japan-U.S. Symposium, Proceedings, Van Nostrand Reinhold Co., 1982.

Synthesis and Properties of the Geometrical Isomers of 1,2,3,4-tetra-tert-butyltetramethylcyclotetrasilane, B. J. Helmer and R. West, Organometal., 1, 1458 (1982).

Peracid Oxidation of the Geometrical Isomers of 1,2,3,4-tetra-tert-butyltetramethylcyclotetrasilane, B. J. Helmer and R. West, Organometal., 1, 1463 (1982).

Publications from this grant:

Evidence for the Intermediacy of Hexamethyl-1,4-disila-benzene, J. D. Rich and R. West, J. Am. Chem. Soc., 104, 6884-6886 (1982).

Orbital Symmetry Analysis of the Reaction of Silylenes with Acetylenes and the Dimerization of 1-Silacyclopropenes, E. A. Halevi and R. West, J. Organometal. Chem., 240, 129-141 (1982).

Electronic Structure of the Silicon-Silicon Double Bond: ^{29}Si NMR Shielding Anisotropy in Tetramesityldisilene, K. W. Zilm, M. J. Fink, D. M. Grant, R. West and J. Michl, Organometal., 2, 193-194 (1983).

Publications in Press

Polysilastyrene: Phenylmethylsilane-Dimethylsilane Copolymers as Precursors to Silicon Carbide, R. West, L. D. David, P. I. Djurovich, H. Yu and R. Sinclair, J. Am. Ceram. Soc.

Formation of Cyclic Silicon-Silicon Systems, R. West in "Inorganic Reactions and Methods," J. J. Zuckerman, ed., Verlag Chemie.

Organosilicon Rotanes: Synthesis and Unexpected Rearrangement, C. W. Carlson and R. West, Organometal.

²⁹Si-NMR of Pentacoordinate Silicon Derivatives, B. J. Helmer, R. West, R. J. P. Corriu, M. Poirier, G. Royo and A. De Saxce, J. Organometal. Chem.

Isomers of (PhMeSi)₆ and (PhMeSi)₅, S.-M. Chen, L. D. David, K. J. Haller, C. L. Wadsworth and R. West, Organometal.

Chemical Reactions of Tetramesityldisilene, M. J. Fink, D. J. De Young, R. West and J. Michl, J. Am. Chem. Soc.

ESR Studies of 1,4-Disilacyclohexa-2,5-diene Free Radical Reactions, J. D. Rich and R. West, J. Am. Chem. Soc.

Table 1
Yields and Molecular Weight Distributions by GPC
for Organosilane Homopolymers

Polymer	% Yield	$\bar{M}_w \times 10^{-3}^a$	Appearance
(PhSiMe) _n	55	193, 5.6	colorless glass
(p-TolSiMe) _n	25		yellow glass
(PhCH ₂ CH ₂ SiMe) _n	35	286, 4.4	colorless glass
(<u>n</u> -PrSiMe) _n	32	644, 13	colorless glass
(<u>n</u> -BuSiMe) _n	34	110, 6	elastomer
(<u>n</u> -HexSiMe) _n	11	524, 21	elastomer
(<u>n</u> -C ₁₂ H ₂₃ SiMe) _n	8	483	waxy solid

^aMaxima of peaks in GPC elution profile.

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Table 2
 Properties of Polysilane Copolymers
 Containing Me₂Si Units, [(XYSi)_m(Me₂Si)_n]_x

X,Y	Yield %	$\bar{M}_n \times 10^3$ ^a	m/n ^b
n-Hexyl, CH ₃	57	170 10	0.66
cyclohexyl, CH ₃	63	900 70 9	0.66
cyclo(CH ₂) ₅	45	70 13 5	1.04
p-Tolyl, CH ₃	51	170 8	0.91
β-Phenethyl, CH ₃	59	330 7	0.65
Phenyl, Phenyl	70	350 4	0.88

^aMaxima of peaks in GPC elution profile.

^bEstimated from integration of proton signals in NMR spectrum.